Technical Report No. 32-673

Two-Center Coulomb Integrals

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ABSTRACT

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One of the difficulties in the application of nonrelativistic quantum mechanics to molecular systems has been the evaluation of the integrals that arise from the use of trial wavefunctions. The present investigation is concerned with a derivation and expression for the general two-center Coulomb integral (over Slater-type atomic orbitals) based on the Fourier-convolution method. All of the Coulomb integrals through N = 4 are given in explicit form in terms of an auxiliary function $W^{p,q}_{m,n}$ which is a simple one-dimensional integral.

Author

I. INTRODUCTION

One of the major problems in the application of nonrelativistic quantum mechanics to molecular systems for the past few decades has been the evaluation of the integrals that arise from the use of trial wavefunctions. If these wavefunctions are expanded in terms of Slater-type atomic orbitals, one needs to evaluate one- and two-electron integrals associated with orbitals on one, two, three, and four different atomic centers. Although the one-center integrals can be evaluated rather easily, the evaluation of the two-electron, two-center integrals that appear (as, for example, the Coulomb, exchange and hybrid integrals) is still a difficult task. Recently, Ruedenberg (Ref. 1) has pursued an approach by which all the many-center integrals can be reduced to the evaluation of a few of the simpler two-center integrals, the Coulomb integrals. However, even for the relatively simple two-center Coulomb integrals, a general analytical treatment has been unavailable until recently.

Roothaan (Ref. 2,3) made the first unified attempt in 1951 to evaluate all the two-center Coulomb integrals that arise from the use of 1s, 2s, and 2p Slater-type atomic orbitals and gave explicit forms. Other specific Coulomb integrals have been given in explicit form by Lofthus (Ref. 4), Preuss (Ref. 5), and Kotani (Ref. 6). More recently, Wahl, Cade, and Roothaan (Ref. 7) have devised a general method for the evaluation of the Coulomb and hybrid integrals, which involves an analytical integration over the coordinates of the first electron and then a double numerical integration over the second electron to obtain the result. Finally, an analytical approach has been given by Ruedenberg and O-Ohata (Ref. 8), which is based on the observation that the Coulomb integral C and the corresponding overlap integral S are related by Poisson's equation $\Delta C = -4\pi S$. Using the analytical result for the overlap integral given by Ruedenberg, O-Ohata, and Wilson (Ref. 9), Ruedenberg and O-Ohata solved Poisson's equation and obtained the Coulomb integral C expressible in terms of a set of auxiliary functions related to integrals over confluent hypergeometric functions (Ref. 10).

The present investigation is concerned with an alternative derivation and expression for the Coulomb integral, based on the Fourier-convolution method introduced by Prosser and Blanchard (Ref. 11) for one-electron, two-center integrals and used by the author for one-electron, two-center integrals over solid spherical harmonics (Ref. 12) and later extended to two-electron, one- and two-center integrals (Ref. 13) and to the two-electron integrals that arise in the evaluation of zero-field splitting (Ref. 14).

II. EVALUATION OF THE COULOMB INTEGRAL

The Coulomb integral

$$C_{NLM}^{N'L'M'}(p_a, p_b; R) = [NLM_a \mid N'L'M_b'] = \int [NLM]_{a1} \frac{1}{r_{12}} [N'L'M']_{b2} \, d\tau_1 \, d\tau_2 \tag{1}$$

where $[NLM]$ is the basic charge distribution, defined by Roothaan (Ref. 2) as

$$[NLM] = \left(\frac{2L+1}{4\pi}\right)^{1/2} \frac{2^L p^{N+2}}{(N+L+1)!} r^{N-1} \exp(-pr) \, S_{L,M}(\theta, \phi) \tag{2}$$

and

$$S_{L,0}(\theta, \phi) = \left(\frac{2L+1}{4\pi}\right)^{1/2} P_L(\cos\theta)$$

$$S_{L,\pm|M|}(\theta, \phi) = \left[\frac{2L+1}{2\pi} \cdot \frac{(L-|M|)!}{(L+|M|)!}\right]^{1/2} P_L^{|M|}(\cos\theta) \begin{Bmatrix} \cos |M|\phi \\ \sin |M|\phi \end{Bmatrix} \tag{3}$$

is equivalent, by the convolution theorem, to

$$(2\pi)^{-3} \int [NLM]_{a1}^{T} \left(\frac{1}{r_{12}}\right)^{T} [N'L'M']_{b2}^{T} \, e^{-i\mathbf{K}\cdot\mathbf{R}} \, d\mathbf{K} \tag{4}$$

where the superscript refers to the Fourier transform, i.e.,

$$f(r)^T = \int e^{i\mathbf{K}\cdot\mathbf{r}} f(\mathbf{r}) \, d\mathbf{r} \tag{5}$$

The transform of the basic charge distribution $[NLM]$ has been given by the author (Ref. 12) and is

$$[NLM]^T = A \frac{P_L^{|M|}(\cos u)\begin{Bmatrix}\cos |M|v \\ \sin |M|v\end{Bmatrix}}{(p^2+K^2)^{N+1}} \sum_{s=0}^{[\frac{1}{2}(N-L)]} (-1)^s \binom{N+L+1}{2s+2L+1} (s+1)_L \left(\frac{K}{p}\right)^{2s+L} \tag{6}$$

where

$$A = \frac{2^{2L+1}\, i^L\, p^{2N+2}}{(2L)!\binom{N+L+1}{2L+1}} \left[\frac{(L-|M|)!}{(L+|M|)!}\right]^{\frac{1}{2}} \left[2\left(1+\delta_{M,0}\right)\right]^{-\frac{1}{2}}$$

$[X]$ means the largest integer in X

$(s+1)_L = (s+L)!/s!$

$\binom{a}{b} = \frac{a!}{b!(a-b)!}$ is the binomial coefficient

K, u, v are the spherical coordinates of $\mathbf{K}$

Table 1 lists the transforms of $[NLM]$ for $N = 1, 2, 3,$ and 4, using the standard notation (Ref. 2) $L = 0, 1, 2, 3 \cdots$ called $S, P, D, F \cdots$ and $M = 0, 1, 2, 3 \cdots$ called $\Sigma, \Pi, \Delta, \Phi \cdots$. For a negative value of M, a bar is placed over the appropriate symbol (e.g., $M = -2$ is $\bar{\Delta}$). The transform of r_{12}^{-1} is simply given by $4\pi K^{-2}$. Integrating over the angular coordinates u and v of $\mathbf{K}$, simplifying the binomial coefficients and rearranging the resulting expression, we have

$$C_{NLM}^{N'L'M'} = (-1)^M \delta_{M,M'} \pi^{-1} \frac{2^{2L+2L'+1} p_a^{2N-L+2} p_b^{2N'-L'+2}}{(2L)!(2L')! \sqrt{(2L+1)(2L'+1)}} \sum_{S=0}^{[\frac{1}{2}(N-L)]} \sum_{t=0}^{[\frac{1}{2}(N'-L')]}$$

$$\times (-1)^{s+t} \frac{(N-L-2s+1)_{2s}}{(2L+2)_{2s}} \frac{(N'-L'-2t+1)_{2t}}{(2L'+2)_{2t}} \frac{(s+1)_L}{p_a^{2s}} \frac{(t+1)_{L'}}{p_b^{2t}} \sum_{r=0}^{L<} \tag{7}$$

$$\times (-1)^r (2L+2L'-4r+1) C^{L+L'-2r}(LM;L'M) \int_0^\infty \frac{K^{2s+2t+L+L'} j_{L+L'-2r}(KR)\, dK}{(K^2+p_a^2)^{N+1}(K^2+p_b^2)^{N'+1}}$$

where $L_<$ is the lesser of L and L', $j_p(x)$ are the spherical Bessel functions (Ref. 10), and $C^l(LM;L'M)$ are the Condon-Shortley coefficients as given by Slater (Ref. 15), as

$$C^l(LM;L'M) = \frac{1}{2}\left[\frac{(L-|M|)!(2L+1)(L'-|M|)!(2L'+1)}{(L+|M|)!(L'+|M|)!}\right]^{\frac{1}{2}} \int_0^\pi P_L^{|M|}(\cos u)\, P_{L'}^{|M|}(\cos u)$$

$$\times P_l(\cos u) \sin u \, du \tag{8}$$

Finally, introducing the coefficients

$$Q_L^{L'} = \frac{2^{2L+2L'+1} p_a^{-L} p_b^{-L'}}{(2L)!(2L')! [(2L+1)(2L'+1)]^{\frac{1}{2}}}$$

$$S_{N,L}(s) = \frac{(N-L-2s+1)_{2s}}{(2L+2)_{2s}} \frac{(s+1)_L}{p_a^{2s}} \tag{9}$$

and

$$T_{N',L'}(t) = \frac{(N' - L' - 2t + 1)_{2t}}{(2L' + 2)_{2t}} \; \frac{(t+1)_{L'}}{p_b^{2t}}$$

and the auxiliary function

$$W_{m,n}^{p,q}(p_a, p_b; R) = \pi^{-1} p_a^{2p} p_b^{2q} \int_0^{\infty} \frac{K^{m+2n} j_m(KR)\, dK}{(K^2 + p_a^2)^p (K^2 + p_b^2)^q} \tag{10}$$

we obtain as the result for the general Coulomb integral

$$C_{NLM}^{N'L'M'}(p_a, p_b; R) = (-1)^M \delta_{M,M'} Q_L^{L'} \sum_{s=0}^{[\frac{1}{2}(N-L)]} \sum_{t=0}^{[\frac{1}{2}(N'-L')]} (-1)^{s+t} \; _{N,L}(s)\, T_{N',L'}(t) \sum_{r=0}^{L_<}$$

$$\times (-1)^r (2L + 2L' - 4r + 1)\, C^{L+L'-2r}(LM;L'M')\, W_{L+L'-2r,\; s+t+r}^{N+1,N'+1}(p_a, p_b; R) \tag{11}$$

III. DISCUSSION

The expression for the Coulomb integral Eq. (11) involves a triple summation over the indices s, t, and r. The summation is over only a limited number of terms, as, for example, for $N = N' = 5$, the maximum number of terms arising is 18 (when $L = L' = 1$). Often, the number of terms is further lowered by the use of the recurrence relation for the spherical Bessel functions

$$j_{n-1}(x) + j_{n+1}(x) = \frac{(2n+1)}{x} j_n(x) \tag{12}$$

We also note from Eq. (11) that the Coulomb integral vanishes if M and M' are different, and that the integral is independent of M, i.e., Roothaan's Theorem II (Ref. 2).

For a given value of $N = N'$, the number of different Coulomb integrals that arise is

$$\frac{1}{120} N(N+1)(N+2)(3N^2 + 6N + 11) \tag{13}$$

Table 2 gives all 83 Coulomb integrals (through $N = 4$) in terms of the auxiliary function W defined by Eq. (10). The final difficulty is the one-dimensional infinite integral over K. Although this integral can be evaluated analytically (by using the techniques used for the evaluation of auxiliary functions $A(2m; p,q)$ and $B(2m+1; p, q)$ of Ref. 14), the result is rather cumbersome and, in fact, the integration can simply and rapidly be done numerically. Moreover, retaining the integral and evaluating it numerically allows one to either let the charges be equal ($p_a = p_b$) or let the distance R be zero (one-center Coulomb integral), or both, with no additional complications if we recognize that

$$j_p(0) = \delta_{p,0} \tag{14}$$

Some recurrence relations that may be useful for the W functions are

$$W_{m,r}^{p,q} = p_a^2 \, [W_{m,r-1}^{p-1,q} - W_{m,r-1}^{p,q}]$$

$$W_{m,r}^{p,q} = p_b^2 \, [W_{m,r-1}^{p,q-1} - W_{m,r-1}^{p,q}]$$

and

$$W_{m,r}^{p,q} = \frac{R}{(2m+1)} \, [W_{m+1,r}^{p,q} + W_{m-1,r+1}^{p,q}] \tag{15}$$

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Table 1. Transforms of [NLM] for N = 1, 2, 3, and 4

$$[1S]^T = p^4 (k^2 + p^2)^{-2}$$

$$[2S]^T = \frac{1}{3} p^4 \left[4p^2 (k^2 + p^2)^{-3} - (k^2 + p^2)^{-2}\right]$$

$$\left.\begin{matrix}[2P\Sigma]^T \\ [2P\Pi]^T \\ [2P\bar{\Pi}]^T\end{matrix}\right\} = 2ik\, p^5 (k^2 + p^2)^{-3} \left\{\begin{matrix} P_1 (\cos u) \\ P_1^1 (\cos u) \cos v \\ P_1^1 (\cos u) \sin v\end{matrix}\right.$$

$$[3S]^T = p^6 \left[2p^2 (k^2 + p^2)^{-4} - (k^2 + p^2)^{-3}\right]$$

$$\left.\begin{matrix}[3P\Sigma]^T \\ [3P\Pi]^T \\ [3P\bar{\Pi}]^T\end{matrix}\right\} = \frac{2}{5}\, ik\, p^5 \left[6p^2 (k^2 + p^2)^{-4} - (k^2 + p^2)^{-3}\right] \left\{\begin{matrix} P_1 (\cos u) \\ P_1^1 (\cos u) \cos v \\ P_1^1 (\cos u) \sin v\end{matrix}\right.$$

$$\left.\begin{matrix}[3D\Sigma]^T \\ [3D\Pi]^T \\ [3D\bar{\Pi}]^T \\ [3D\Delta]^T \\ [3D\bar{\Delta}]^T\end{matrix}\right\} = \frac{2}{9} \sqrt{3}\, p^6 \left[p^2 (k^2 + p^2)^{-4} - (k^2 + p^2)^{-3}\right] \left\{\begin{matrix} 2\sqrt{3}\, P_2 (\cos u) \\ 2\, P_2^1 (\cos u) \cos v \\ 2\, P_2^1 (\cos u) \sin v \\ P_2^2 (\cos u) \cos 2v \\ P_2^2 (\cos u) \sin 2v\end{matrix}\right.$$

$$[4S]^T = \frac{1}{5} p^6 \left[16\, p^4 (k^2 + p^2)^{-5} - 12\, p^2 (k^2 + p^2)^{-4} + (k^2 + p^2)^{-3}\right]$$

$$\left.\begin{matrix}[4P\Sigma]^T \\ [4P\Pi]^T \\ [4P\bar{\Pi}]^T\end{matrix}\right\} = \frac{2}{5}\, ik\, p^7 \left[8\, p^2 (k^2 + p^2)^{-5} - 3\, (k^2 + p^2)^{-4}\right] \left\{\begin{matrix} P_1 (\cos u) \\ P_1^1 (\cos u) \cos v \\ P_1^1 (\cos u) \sin v\end{matrix}\right.$$

Table 1 (Cont'd)

$$\left.\begin{array}{l}[4D\Sigma]^T\\ [4D\Pi]^T\\ [4D\bar{\Pi}]^T\\ [4D\Delta]^T\\ [4D\bar{\Delta}]^T\end{array}\right\} = \frac{2}{63}\sqrt{3}\,p^6\,[8\,p^4(k^2+p^2)^{-5} - 9\,p^2(k^2+p^2)^{-4} + (k^2+p^2)^{-3}]\left\{\begin{array}{l}2\sqrt{3}\,P_2(\cos u)\\ 2\,P_2^1(\cos u)\cos v\\ 2\,P_2^1(\cos u)\sin v\\ P_2^2(\cos u)\cos 2v\\ P_2^2(\cos u)\sin 2v\end{array}\right.$$

$$\left.\begin{array}{l}[4F\Sigma]^T\\ [4F\Pi]^T\\ [4F\bar{\Pi}]^T\\ [4F\Delta]^T\\ [4F\bar{\Delta}]^T\\ [4F\Phi]^T\\ [4F\bar{\Phi}]^T\end{array}\right\} = \frac{2}{225}\sqrt{10}\,ik\,p^7\,[p^2(k^2+p^2)^{-5} - (k^2+p^2)^{-4}]\left\{\begin{array}{l}6\sqrt{10}\,P_3(\cos u)\\ 2\sqrt{15}\,P_3^1(\cos u)\cos v\\ 2\sqrt{15}\,P_3^1(\cos u)\sin v\\ \sqrt{6}\,P_3^2(\cos u)\cos 2v\\ \sqrt{6}\,P_3^2(\cos u)\sin 2v\\ P_3^3(\cos u)\cos 3v\\ P_3^3(\cos u)\sin 3v\end{array}\right.$$

Table 2. Coulomb integrals expressed in terms of auxiliary function W^*

$$[1\,S_a|1\,S_b] = 2\,W_{00}^{22}$$

$$[1\,S_a|2\,S_b] = 2\left[W_{00}^{23} - \frac{1}{3}\,p_b^{-2}\,W_{01}^{23}\right]$$

$$[1\,S_a|3\,S_b] = 2[W_{00}^{24} - p_b^{-2}\,W_{01}^{24}]$$

$$[1\,S_a|4\,S_b] = 2\left[W_{00}^{25} - 2\,p_b^{-2}\,W_{01}^{25} + \frac{1}{5}\,p_b^{-4}\,W_{02}^{25}\right]$$

$$[2\,S_a|2\,S_b] = 2\left[W_{00}^{33} - \frac{1}{3}\,(p_a^{-2} + p_b^{-2})\,W_{01}^{33} + \frac{1}{9}\,p_a^{-2}\,p_b^{-2}\,W_{02}^{33}\right]$$

$$[2\,S_a|3\,S_b] = 2\left[W_{00}^{34} - \left(\frac{1}{3}\,p_a^{-2} + p_b^{-2}\right)\,W_{01}^{34} + \frac{1}{3}\,p_a^{-2}\,p_b^{-2}\,W_{02}^{34}\right]$$

$$[2\,S_a|4\,S_b] = 2\left[W_{00}^{35} - \left(\frac{1}{3}\,p_a^{-2} + 2\,p_b^{-2}\right)\,W_{01}^{35} + \left(\frac{2}{3}\,p_a^{-2} + \frac{1}{5}\,p_b^{-2}\right)\,p_b^{-2}\,W_{02}^{35}\right.$$
$$\left.- \frac{1}{15}\,p_a^{-2}\,p_b^{-4}\,W_{03}^{35}\right]$$

$$[3\,S_a|3\,S_b] = 2[W_{00}^{44} - (p_a^{-2} + p_b^{-2})\,W_{01}^{44} + p_a^{-2}\,p_b^{-2}\,W_{02}^{44}]$$

$$[3\,S_a|4\,S_b] = 2\left[W_{00}^{45} - (p_a^{-2} + 2\,p_b^{-2})\,W_{01}^{45} + \left(2\,p_a^{-2} + \frac{1}{5}\,p_b^{-2}\right)\,p_b^{-2}\,W_{02}^{45} - \frac{1}{5}\,p_a^{-2}\,p_b^{-4}\,W_{03}^{45}\right]$$

$$[4\,S_a|4\,S_b] = 2\left[W_{00}^{55} - 2\,(p_a^{-2} + p_b^{-2})\,W_{01}^{55} + \left(\frac{1}{5}\,p_a^{-4} + 4\,p_a^{-2}\,p_b^{-2} + \frac{1}{5}\,p_b^{-4}\right)\,W_{02}^{55}\right.$$
$$\left.- \frac{2}{5}\,(p_a^{-2} + p_b^{-2})\,p_a^{-2}\,p_b^{-2}\,W_{03}^{55} + \frac{1}{25}\,p_a^{-4}\,p_b^{-4}\,W_{04}^{55}\right]$$

*In the above table, $W_{m,n}^{p,q}\,(p_a, p_b; R)$ is abbreviated to W_{mn}^{pq}.

Table 2 (Cont'd)

$$[1S_a|2P\Sigma_b] = 4\,p_b^{-1}\,W_{10}^{23}$$

$$[1S_a|3P\Sigma_b] = 4\,p_b^{-1}\left[W_{10}^{24} - \frac{1}{5}\,p_b^{-2}\,W_{11}^{24}\right]$$

$$[1S_a|4P\Sigma_b] = 4\,p_b^{-1}\left[W_{10}^{25} - \frac{2}{5}\,p_b^{-2}\,W_{11}^{25}\right]$$

$$[2S_a|2P\Sigma_b] = 4\,p_b^{-1}\left[W_{10}^{33} - \frac{1}{3}\,p_a^{-2}\,W_{11}^{33}\right]$$

$$[2S_a|3P\Sigma_b] = 4\,p_b^{-1}\left[W_{10}^{34} - \left(\frac{1}{3}\,p_a^{-2} + \frac{1}{5}\,p_b^{-2}\right)\,W_{11}^{34} + \frac{1}{15}\,p_a^{-2}\,p_b^{-2}\,W_{12}^{34}\right]$$

$$[2S_a|4P\Sigma_b] = 4\,p_b^{-1}\left[W_{10}^{35} - \left(\frac{1}{3}\,p_a^{-2} + \frac{3}{5}\,p_b^{-2}\right)\,W_{11}^{35} + \frac{1}{5}\,p_a^{-2}\,p_b^{-2}\,W_{12}^{35}\right]$$

$$[3S_a|2P\Sigma_b] = 4\,p_b^{-1}\,[W_{10}^{43} - p_a^{-2}\,W_{11}^{43}]$$

$$[3S_a|3P\Sigma_b] = 4\,p_b^{-1}\left[W_{10}^{44} - \left(p_a^{-2} + \frac{1}{5}\,p_b^{-2}\right)\,W_{11}^{44} + \frac{1}{5}\,p_a^{-2}\,p_b^{-2}\,W_{12}^{44}\right]$$

$$[3S_a|4P\Sigma_b] = 4\,p_b^{-1}\left[W_{10}^{45} - \left(p_a^{-2} + \frac{3}{5}\,p_b^{-2}\right)\,W_{11}^{45} + \frac{3}{5}\,p_a^{-2}\,p_b^{-2}\,W_{12}^{45}\right]$$

$$[4S_a|2P\Sigma_b] = 4\,p_b^{-1}\left[W_{10}^{53} - 2\,p_a^{-2}\,W_{11}^{53} + \frac{1}{5}\,p_a^{-4}\,W_{12}^{53}\right]$$

$$[4S_a|3P\Sigma_b] = 4\,p_b^{-1}\left[W_{10}^{54} - \left(2\,p_a^{-2} + \frac{1}{5}\,p_b^{-2}\right)\,W_{11}^{54} + \frac{1}{5}\,(p_a^{-2} + 2\,p_b^{-2})\,p_a^{-2}\,W_{12}^{54} - \frac{1}{25}\,p_a^{-4}\,p_b^{-2}\,W_{13}^{54}\right]$$

$$[4S_a|4P\Sigma_b] = 4\,p_b^{-1}\left[W_{10}^{55} - \left(2\,p_a^{-2} + \frac{3}{5}\,p_b^{-2}\right)\,W_{11}^{55} + \frac{1}{5}\,(p_a^{-2} + 6\,p_b^{-2})\,p_a^{-2}\,W_{12}^{55} - \frac{3}{25}\,p_a^{-4}\,p_b^{-2}\,W_{13}^{55}\right]$$

Table 2 (Cont'd)

$$[1S_a|3\,D\Sigma_b] = \frac{8}{3}\, p_b^{-2}\, W_{20}^{24}$$

$$[1S_a|4\,D\Sigma_b] = \frac{8}{3}\, p_b^{-2} \left[W_{20}^{25} - \frac{1}{7}\, p_b^{-2}\, W_{21}^{25}\right]$$

$$[2S_a|3\,D\Sigma_b] = \frac{8}{3}\, p_b^{-2} \left[W_{20}^{34} - \frac{1}{3}\, p_a^{-2}\, W_{21}^{34}\right]$$

$$[2S_a|4\,D\Sigma_b] = \frac{8}{3}\, p_b^{-2} \left[W_{20}^{35} - \left(\frac{1}{3}\, p_a^{-2} + \frac{1}{7}\, p_b^{-2}\right) W_{21}^{35} + \frac{1}{21}\, p_a^{-2}\, p_b^{-2}\, W_{22}^{35}\right]$$

$$[3S_a|3\,D\Sigma_b] = \frac{8}{3}\, p_b^{-2} \left[W_{20}^{44} - p_a^{-2}\, W_{21}^{44}\right]$$

$$[3S_a|4\,D\Sigma_b] = \frac{8}{3}\, p_b^{-2} \left[W_{20}^{45} - \left(p_a^{-2} + \frac{1}{7}\, p_b^{-2}\right) W_{21}^{45} + \frac{1}{7}\, p_a^{-2}\, p_b^{-2}\, W_{22}^{45}\right]$$

$$[4S_a|3\,D\Sigma_b] = \frac{8}{3}\, p_b^{-2} \left[W_{20}^{54} - 2\, p_a^{-2}\, W_{21}^{54} + \frac{1}{5}\, p_a^{-4}\, W_{22}^{54}\right]$$

$$[4S_a|4\,D\Sigma_b] = \frac{8}{3}\, p_b^{-2} \left[W_{20}^{55} - \left(2\, p_a^{-2} + \frac{1}{7}\, p_b^{-2}\right) W_{21}^{55} + \left(\frac{1}{5}\, p_a^{-2} + \frac{2}{7}\, p_b^{-2}\right) p_a^{-2}\, W_{22}^{55} - \frac{1}{35}\, p_a^{-4}\, p_b^{-2}\, W_{23}^{55}\right]$$

$$[1S_a|4\,F\Sigma_b] = \frac{16}{15}\, p_b^{-3}\, W_{30}^{25}$$

$$[2S_a|4\,F\Sigma_b] = \frac{16}{15}\, p_b^{-3} \left[W_{30}^{35} - \frac{1}{3}\, p_a^{-2}\, W_{31}^{35}\right]$$

$$[3S_a|4\,F\Sigma_b] = \frac{16}{15}\, p_b^{-3}\, [W_{30}^{45} - p_a^{-2}\, W_{31}^{45}]$$

$$[4S_a|4\,F\Sigma_b] = \frac{16}{15}\, p_b^{-3} \left[W_{30}^{55} - 2\, p_a^{-2}\, W_{31}^{55} + \frac{1}{5}\, p_a^{-4}\, W_{32}^{55}\right]$$

Table 2 (Cont'd)

$$[2P\Sigma_a|2P\Sigma_b] = \frac{8}{3} p_a^{-1} p_b^{-1} [2W_{20}^{33} - W_{01}^{33}]$$

$$[2P\Sigma_a|3P\Sigma_b] = \frac{8}{3} p_a^{-1} p_b^{-1} \left[(2W_{20}^{34} - W_{01}^{34}) - \frac{1}{5} p_b^{-2} (2W_{21}^{34} - W_{02}^{34})\right]$$

$$[2P\Sigma_a|4P\Sigma_b] = \frac{8}{3} p_a^{-1} p_b^{-1} \left[(2W_{20}^{35} - W_{01}^{35}) - \frac{3}{5} p_b^{-2} (2W_{21}^{35} - W_{02}^{35})\right]$$

$$[3P\Sigma_a|3P\Sigma_b] = \frac{8}{3} p_a^{-1} p_b^{-1} \left[(2W_{20}^{44} - W_{01}^{44}) - \frac{1}{5} (p_a^{-2} + p_b^{-2})(2W_{21}^{44} - W_{02}^{44}) + \frac{1}{25} p_a^{-2} p_b^{-2} (2W_{22}^{44} - W_{03}^{44})\right]$$

$$[3P\Sigma_a|4P\Sigma_b] = \frac{8}{3} p_a^{-1} p_b^{-1} \left[(2W_{20}^{45} - W_{01}^{45}) - \frac{1}{5}(p_a^{-2} + 3p_b^{-2}) (2W_{21}^{45} - W_{02}^{45}) + \frac{3}{25} p_a^{-2} p_b^{-2} (2W_{22}^{45} - W_{03}^{45})\right]$$

$$[4P\Sigma_a|4P\Sigma_b] = \frac{8}{3} p_a^{-1} p_b^{-1} \left[(2W_{20}^{55} - W_{01}^{55}) - \frac{3}{5} (p_a^{-2} + p_b^{-2}) (2W_{21}^{55} - W_{02}^{55}) + \frac{9}{25} p_a^{-2} p_b^{-2} (2W_{22}^{55} - W_{03}^{55})\right]$$

$$[2P\Sigma_a|3D\Sigma_b] = \frac{16}{15} p_a^{-1} p_b^{-2} [3W_{30}^{34} - 2W_{11}^{34}]$$

$$[2P\Sigma_a|4D\Sigma_b] = \frac{16}{15} p_a^{-1} p_b^{-2} \left[(3W_{30}^{35} - 2W_{11}^{35}) - \frac{1}{7} p_b^{-2} (3W_{31}^{35} - 2W_{12}^{35})\right]$$

$$[3P\Sigma_a|3D\Sigma_b] = \frac{16}{15} p_a^{-1} p_b^{-2} \left[(3W_{30}^{44} - 2W_{11}^{44}) - \frac{1}{5} p_a^{-2} (3W_{31}^{44} - 2W_{12}^{44})\right]$$

Table 2 (Cont'd)

$$[3\,P\Sigma_a\,|\,4\,D\Sigma_b] = \frac{16}{15}\,p_a^{-1}\,p_b^{-2}\left[(3\,W_{30}^{45} - 2\,W_{11}^{45}) - \left(\frac{1}{5}\,p_a^{-2} + \frac{1}{7}\,p_b^{-2}\right)(3\,W_{31}^{45} - 2\,W_{12}^{45}) + \frac{1}{35}\,p_a^{-2}\,p_b^{-2}\,(3\,W_{32}^{45} - 2\,W_{13}^{45})\right]$$

$$[4\,P\Sigma_a\,|\,3\,D\Sigma_b] = \frac{16}{15}\,p_a^{-1}\,p_b^{-2}\left[(3\,W_{30}^{54} - 2\,W_{11}^{54}) - \frac{3}{5}\,p_a^{-2}\,(3\,W_{31}^{54} - 2\,W_{12}^{54})\right]$$

$$[4\,P\Sigma_a\,|\,4\,D\Sigma_b] = \frac{16}{15}\,p_a^{-1}\,p_b^{-2}\left[(3\,W_{30}^{55} - 2\,W_{11}^{55}) - \left(\frac{3}{5}\,p_a^{-2} + \frac{1}{7}\,p_b^{-2}\right)(3\,W_{31}^{55} - 2\,W_{12}^{55}) + \frac{3}{35}\,p_a^{-2}\,p_b^{-2}\,(3\,W_{32}^{55} + 2\,W_{13}^{55})\right]$$

$$[2\,P\Sigma_a\,|\,4\,F\Sigma_b] = \frac{32}{105}\,p_a^{-1}\,p_b^{-3}\,[4\,W_{40}^{35} - 3\,W_{21}^{35}]$$

$$[3\,P\Sigma_a\,|\,4\,F\Sigma_b] = \frac{32}{105}\,p_a^{-1}\,p_b^{-3}\left[(4\,W_{40}^{45} - 3\,W_{21}^{45}) - \frac{1}{5}\,p_a^{-2}\,(4\,W_{41}^{45} - 3\,W_{22}^{45})\right]$$

$$[4\,P\Sigma_a\,|\,4\,F\Sigma_b] = \frac{32}{105}\,p_a^{-1}\,p_b^{-3}\left[(4\,W_{40}^{55} - 3\,W_{21}^{55}) - \frac{3}{5}\,p_a^{-2}\,(4\,W_{41}^{55} - 3\,W_{22}^{55})\right]$$

$$[3\,D\Sigma_a\,|\,3\,D\Sigma_b] = \frac{32}{315}\,p_a^{-2}\,p_b^{-2}\,[18\,W_{40}^{44} - 10\,W_{21}^{44} + 7\,W_{02}^{44}]$$

$$[3\,D\Sigma_a\,|\,4\,D\Sigma_b] = \frac{32}{315}\,p_a^{-2}\,p_b^{-2}\left[(18\,W_{40}^{45} - 10\,W_{21}^{45} + 7\,W_{02}^{45}) - \frac{1}{7}\,p_b^{-2}\,(18\,W_{41}^{45} - 10\,W_{22}^{45} + 7\,W_{03}^{45})\right]$$

$$[4\,D\Sigma_a\,|\,4\,D\Sigma_b] = \frac{32}{315}\,p_a^{-2}\,p_b^{-2}\left[(18\,W_{40}^{55} - 10\,W_{21}^{55} + 7\,W_{02}^{55}) - \frac{1}{7}\,(p_a^{-2}+p_b^{-2})(18\,W_{41}^{55} - 10\,W_{22}^{55} + 7\,W_{03}^{55}) + \frac{1}{49}\,p_a^{-2}\,p_b^{-2}\,(18\,W_{42}^{55} - 10\,W_{23}^{55} + 7\,W_{04}^{55})\right]$$

Table 2 (Cont'd)

$$[3D\Sigma_a|4F\Sigma_b] = \frac{64}{4725}\, p_a^{-2}\, p_b^{-3}\, [50\, W_{50}^{45} - 28\, W_{31}^{45} + 27\, W_{12}^{45}]$$

$$[4D\Sigma_a|4F\Sigma_b] = \frac{64}{4725}\, p_a^{-2}\, p_b^{-3} \left[(50\, W_{50}^{55} - 28\, W_{31}^{55} + 27\, W_{12}^{55}) - \frac{1}{7}\, p_a^{-2}\, (50\, W_{51}^{55} - 28\, W_{32}^{55} + 27\, W_{13}^{55})\right]$$

$$[4F\Sigma_a|4F\Sigma_b] = \frac{128}{1575}\, p_a^{-3}\, p_b^{-3} \left[\frac{100}{33}\, W_{60}^{55} - \frac{18}{11}\, W_{41}^{55} + \frac{4}{3}\, W_{22}^{55} - W_{03}^{55}\right]$$

$$[2P\Pi_a|2P\Pi_b] = 8\, p_a^{-1}\, p_b^{-1}\, W_{10}^{33}$$

$$[2P\Pi_a|3P\Pi_b] = 8\, p_a^{-1}\, p_b^{-1} \left[W_{10}^{34} - \frac{1}{5}\, p_b^{-2}\, W_{11}^{34}\right]$$

$$[2P\Pi_a|4P\Pi_b] = 8\, p_a^{-1}\, p_b^{-1} \left[W_{10}^{35} - \frac{3}{5}\, p_b^{-2}\, W_{11}^{35}\right]$$

$$[3P\Pi_a|3P\Pi_b] = 8\, p_a^{-1} p_b^{-1} \left[W_{10}^{44} - \frac{1}{5}\, (p_a^{-2} + p_b^{-2})\, W_{11}^{44} + \frac{1}{25}\, p_a^{-2}\, p_b^{-2}\, W_{12}^{44}\right]$$

$$[3P\Pi_a|4P\Pi_b] = 8\, p_a^{-1}\, p_b^{-1} \left[W_{10}^{45} - \frac{1}{5}\, (p_a^{-2} + 3\, p_b^{-2})\, W_{11}^{45} + \frac{3}{25}\, p_a^{-2}\, p_b^{-2}\, W_{12}^{45}\right]$$

$$[4P\Pi_a|4P\Pi_b] = 8\, p_a^{-1}\, p_b^{-1} \left[W_{10}^{55} - \frac{3}{5}\, (p_a^{-2} + p_b^{-2})\, W_{11}^{55} + \frac{9}{25}\, p_a^{-2}\, p_b^{-2}\, W_{12}^{55}\right]$$

$$[2P\Pi_a|3D\Pi_b] = \frac{16}{3}\, \sqrt{3}\, p_a^{-1}\, p_b^{-2}\, W_{20}^{34}$$

$$[2P\Pi_a|4D\Pi_b] = \frac{16}{3}\, \sqrt{3}\, p_a^{-1}\, p_b^{-2} \left[W_{20}^{35} - \frac{1}{7}\, p_b^{-2}\, W_{21}^{35}\right]$$

Table 2 (Cont'd)

$$[3\,P\Pi_a|3\,D\Pi_b] = \frac{16}{3}\sqrt{3}\,p_a^{-1}\,p_b^{-2}\left[W_{20}^{44} - \frac{1}{5}\,p_a^{-2}\,W_{21}^{44}\right]$$

$$[3\,P\Pi_a|4\,D\Pi_b] = \frac{16}{3}\sqrt{3}\,p_a^{-1}\,p_b^{-2}\left[W_{20}^{45} - \left(\frac{1}{5}\,p_a^{-2} + \frac{1}{7}\,p_b^{-2}\right)W_{21}^{45} + \frac{1}{35}\,p_a^{-2}\,p_b^{-2}\,W_{22}^{45}\right]$$

$$[4\,P\Pi_a|3\,D\Pi_b] = \frac{16}{3}\sqrt{3}\,p_a^{-1}\,p_b^{-2}\left[W_{20}^{54} - \frac{3}{5}\,p_a^{-2}\,W_{21}^{54}\right]$$

$$[4\,P\Pi_a|4\,D\Pi_b] = \frac{16}{3}\sqrt{3}\,p_a^{-1}\,p_b^{-2}\left[W_{20}^{55} - \left(\frac{3}{5}\,p_a^{-2} + \frac{1}{7}\,p_b^{-2}\right)W_{21}^{55} + \frac{3}{35}\,p_a^{-2}\,p_b^{-2}\,W_{22}^{55}\right]$$

$$[2\,P\Pi_a|4\,F\Pi_b] = \frac{32}{15}\sqrt{6}\,p_a^{-1}\,p_b^{-3}\,W_{30}^{35}$$

$$[3\,P\Pi_a|4\,F\Pi_b] = \frac{32}{15}\sqrt{6}\,p_a^{-1}\,p_b^{-3}\left[W_{30}^{45} - \frac{1}{5}\,p_a^{-2}\,W_{31}^{45}\right]$$

$$[4\,P\Pi_a|4\,F\Pi_b] = \frac{32}{15}\sqrt{6}\,p_a^{-1}\,p_b^{-3}\left[W_{30}^{55} - \frac{3}{5}\,p_a^{-2}\,W_{31}^{55}\right]$$

$$[3\,D\Pi_a|3\,D\Pi_b] = \frac{32}{15}\,p_a^{-2}\,p_b^{-2}\,[4\,W_{30}^{44} - W_{11}^{44}]$$

$$[3\,D\Pi_a|4\,D\Pi_b] = \frac{32}{15}\,p_a^{-2}\,p_b^{-2}\left[(4\,W_{30}^{45} - W_{11}^{45}) - \frac{1}{7}\,p_b^{-2}\,(4\,W_{31}^{45} - W_{12}^{45})\right]$$

$$[4\,D\Pi_a|4\,D\Pi_b] = \frac{32}{15}\,p_a^{-2}\,p_b^{-2}\left[(4\,W_{30}^{55} - W_{11}^{55}) - \frac{1}{7}\,(p_a^{-2} + p_b^{-2})\,(4\,W_{31}^{55} - W_{12}^{55}) + \frac{1}{49}\,p_a^{-2}\,p_b^{-2}\,(4\,W_{32}^{55} - W_{13}^{55})\right]$$

$$[3\,D\Pi_a|4\,F\Pi_b] = \frac{64}{105}\sqrt{2}\,p_a^{-2}\,p_b^{-3}\,[5\,W_{40}^{45} - 2\,W_{21}^{45}]$$

$$[4\,D\Pi_a|4\,F\Pi_b] = \frac{64}{105}\sqrt{2}\,p_a^{-2}\,p_b^{-3}\left[(5\,W_{40}^{55} - 2\,W_{21}^{55}) - \frac{1}{7}\,p_a^{-2}\,(5\,W_{41}^{55} - 2\,W_{22}^{55})\right]$$

Table 2 (Cont'd)

$$[4\,F\Pi_a \,|\, 4\,F\Pi_b] = \frac{128}{1575}\, p_a^{-3}\, p_b^{-3}\, [25\, W_{50}^{55} - 14\, W_{31}^{55} + 3\, W_{12}^{55}]$$

$$[3\,D\Delta_a \,|\, 3\,D\Delta_b] = \frac{32}{3}\, p_a^{-2}\, p_b^{-2}\, W_{20}^{44}$$

$$[3\,D\Delta_a \,|\, 4\,D\Delta_b] = \frac{32}{3}\, p_a^{-2}\, p_b^{-2} \left[W_{20}^{45} - \frac{1}{7}\, p_b^{-2}\, W_{21}^{45} \right]$$

$$[4\,D\Delta_a \,|\, 4\,D\Delta_b] = \frac{32}{3}\, p_a^{-2}\, p_b^{-2} \left[W_{20}^{55} - \frac{1}{7}\, (p_a^{-2} + p_b^{-2})\, W_{21}^{55} + \frac{1}{49}\, p_a^{-2}\, p_b^{-2}\, W_{22}^{55} \right]$$

$$[3\,D\Delta_a \,|\, 4\,F\Delta_b] = \frac{64}{15}\, \sqrt{5}\, p_a^{-2}\, p_b^{-3}\, W_{30}^{45}$$

$$[4\,D\Delta_a \,|\, 4\,F\Delta_b] = \frac{64}{15}\, \sqrt{5}\, p_a^{-2}\, p_b^{-3} \left[W_{30}^{55} - \frac{1}{7}\, p_a^{-2}\, W_{31}^{55} \right]$$

$$[4\,F\Delta_a \,|\, 4\,F\Delta_b] = \frac{128}{105}\, p_a^{-3}\, p_b^{-3}\, [6\, W_{40}^{55} - W_{21}^{55}]$$

$$[4\,F\Phi_a \,|\, 4\,F\Phi_b] = \frac{128}{15}\, p_a^{-3}\, p_b^{-3}\, W_{30}^{55}$$